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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The feasibility of visible light Fourier transform photoacoustic spectroscopy (FTPAS) is demonstrated. The combined throughput and multiplex advantages of the interferometer significantly reduce the data collection time and/or improve the signal to noise ratio. An FTPAS interferogram and transformed spectrum of neodymium(III) doped glass are reported.

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FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY

by

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April 25, 1978

Fourier transform photoacoustic spectroscopy

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(Abstract)

The feasibility of visible light Fourier transform photoacoustic spectroscopy
(FTPAS) is demonstrated. The combined throughput and multiplex advantages of
the interferometer significantly reduce the data collection time and/or im-
prove the signal to noise ratio. An FTPAS interferogram and transformed spec-
trum of neodymium(III) doped glass are reported.

Photoacoustic spectroscopy[1] (PAS) traces its origins to experiments re-
ported by Alexander Graham Bell[2] in 1881. A periodically chopped beam of
tunable, monochromatic, uv-visible light passes through a window onto a con-
densed phase sample in an enclosed cell. The cell also contains a transpar-
ent gas and a microphone. If the sample absorbs light of the particular inci-
dent wavelength and does not fluoresce, rapid radiationless decay processes
convert the electronic energy to thermal energy that in turn heats the ambient
gas at the sample-gas interface. The heating of the gas produces a sound
wave of the same frequency as the chopping frequency of the incident light
beam. This audio frequency sound wave is detected by the microphone and sorted
out of the environmental and electronic noise by a lock-in amplifier. The
stress wave may also be detected directly in the sample by attaching a
piezoelectric transducer to the sample.[3,4] Thus by varying the wavelength
of the incident light it is possible[5] to obtain a uv-visible absorbance
spectrum of a light transmitting solid or liquid sample that closely re-
sembles that obtained by a more conventional transmission spectrometer.
More important, PAS permits an experimentalist to obtain uv-visible absor-
bance spectra of samples that are opaque[6] as well as of highly transparent
samples of short optical path length.[3]

Regardless of whether one uses a microphone or piezoelectric transducer
as the detector in a PAS experiment, the measurement is detector noise limited.[7]
This is in contrast to the photon detectors used in transmission spectroscopy
in the visible and ultraviolet wavelength ranges. In the latter case, the
photomultipliers used are among the quietest detectors and amplifiers used
in any system; the noise in these systems comes from the radiation source not
the detector. Of course, if the noise is indeed random in the photoacoustic

system, an improved S/N may be obtained by integrating the signal longer, that is, increasing the detection time constant and lowering the spectral scan rate. This accounts for the long time presently required to obtain a photoacoustic spectrum (up to ~1 hour).

A Michelson interferometer allows collection of data from all spectral frequencies simultaneously throughout the duration of the measurement. The resulting interferogram can then be numerically transformed via the Fourier transform back to a conventional spectrum. The improvement in S/N achieved by multiplexing the spectral information and measuring the variations in the much higher intensity is known as Fellgett's advantage. The magnitude of this advantage is determined by the number of spectral resolution elements, M, to be measured. This is given by[8]

$$M = \upsilon_R / \Delta\upsilon_I \qquad (1)$$

where υ_R is the wavenumber range of the measurement and $\Delta\upsilon_I$, the instrumental resolution, in cm^{-1}. For spectra measured in equal times with identical sources, detectors, optical throughput, and sample, the interferometer will theoretically have a S/N which is $\sqrt{M}$ times better. Alternately, if the two spectra are measured with equal S/N, the FT spectrum can theoretically be measured M times faster. Fellgett's advantage applies only to the time necessary to collect the data and not the time necessary to compute and plot the spectrum from the interferogram (~2 to ~10 seconds depending on the available minicomputer.)

The second fundamental advantage of a Fourier transform spectrometer over a grating (dispersive) spectrometer is Jacquinot's advantage and derives from the increased throughput of an interferometer compared to a grating spectrometer. This advantage is given by[8]

$$\theta^I/\theta^G = (A^I \, f \, a \, \upsilon^2 \, 2)/(A^G \, h \, \upsilon_{max} \, \Delta\upsilon) \qquad (2)$$

where θ is the maximum optical throughput of an interferometer (superscript I) or grating spectrometer (superscript G); A is the area of the mirrors in the interferometer (I) or the area of the grating (G); f is the focal length of the collimator; a is the spacing of the lines on the grating; υ is the spectral wavenumber; h is the slit height on the monochromator; υ_{max} is the highest wavenumber in the spectrum and $\Delta\upsilon$ is the spectral resolution.

Application of FTS to visible wavelengths is not carried out routinely since the broad band noise from the source will be added to each spectral component by the interferometer rather than just the noise from the source at that wavelength which is observed with monochromators. Thus if the spectral information to be gathered is a line source, such as atomic emission spectra, the multiplex advantage will improve the S/N of the spectrum even if the detector is source noise limited.[9] Since the noise in photoacoustic detectors is fixed by the detector itself and the associated electronics and is independent of the signal intensity[5] the optimum means of collecting broadband uv-visible photoacoustic spectra should be a Fourier transform system if the optical and mechanical requirements can be met.

At least two commercial PAS instruments are available (from Princeton Applied Research Corporation and Gilford Instrument Laboratories) and both have dispersive elements (monochromators). The optical components in these systems are similar to those we have used in our dispersive PAS system,[4] and so for an illustration of the improvements which are theoretically attainable by using FT optics we will use the specifications for our monochromator (Bausch and Lomb model 33-86-40) in Eqs. 1 and 2.

Fellgett's advantage (Eq. 1) is computed to be 168 for the 300 to 800 nm spectrum with 8 nm resolution. (v_R = 20833 cm^{-1}, Δv = 66 cm^{-1} = 8 nm @ 550 nm.) This means applying only Fellgett's advantage, it should be possible to obtain exactly the same spectrum (using the same detector, source and electronics) in 1/168 the amount of time ($\sim$18 seconds vs. 50 minutes). Alternately, if 50 minutes are used to collect the interferogram, the S/N will be $\sim$13 times better ($\sqrt{168}$). This is indeed a significant improvement, but an additional advantage appears possible due to the increased throughput of the interferometer.

The Bausch and Lomb monochromator has a 5.2 cm square grating with groove spacing of 1.6 x 10^{-4} cm, slit height of 1.2 cm and accepts a 25 cm focal length collimator. For comparison, we choose an interferometer with $\sim$5.1 cm diameter mirrors. The application of Eq. 2 using Δv = 50 cm^{-1}, v_{max} = 33333 cm^{-1} (300 nm), indicates that Jacquinot's advantage should be as large as $\sim$590 at 300 nm and still be $\sim$50% of Fellgett's advantage at 800 nm. Thus dividing the shorter scan time necessary made possible by Fellgett's advantage (18 seconds) by the minimum value of Jacquinot's advantage, one arrives at a minimum time required to collect a 300 to 800 nm spectrum of $\sim$0.22 seconds. It should be reiterated that the resulting FTPAS spectrum will have the same signal to noise ratio as the spectrum collected in 50 minutes using a monochromator.

Although not mentioned in the foregoing, other techniques of multiplexing spectral information are available, but the only other under development which appears to offer similar advantages for PAS is the Hadamard technique.[10] Bard suggested[7] that this technique might improve the S/N of photoacoustic spectra, although the cost may be prohibitive. Commercial Fourier transform

spectrometers for IR are also costly, but Horlick and Yuen[11] point out that, exclusive of computer, an effective interferometer can be constructed for less than $3,000.

Lately, there has been some discussion[12] of the size of Fellgett's advantage for interferometers but the actual magnitude of the S/N improvements achieved by Fourier Transform instruments in the IR have been confirmed and do generally correspond to those expected based on Eqs. 1 and 2.

Figure 1 shows a block diagram of our Michelson interferometer for FTPAS. Modulation of the output light from the interferometer is achieved by driving one of the mirrors sinusoidally at the lock-in reference frequency in lieu of mechanical chopping with a rotating sector as in ordinary PAS. This results in a phase modulated[13] interferogram thus eliminating the large D.C. offset in the detected signal.

For this demonstration of the feasibility of FTPAS, the scan is accomplished by a total of 11.5 μm change (two times the actual mechanical travel) in one arm of the interferometer. This is the maximum motion possible using the Burleigh PZAT-90 while it also provides the phase modulation. For these experiments, no simultaneous fringe referencing system was used and voltage-motion linearity of the PZAT-90 was assumed.

Figure 2a shows the unreferenced FTPAS interferogram obtained with a sample of Owens-Illinois neodymium(III) doped laser glass. Fig. 2b shows the transformed FTPAS spectrum (not source intensity normalized) which agrees in its broad features with published[4,14] absorption spectra of neodymium(III) doped glass. Although no signal to noise comparison has been made, it should be noted that our previous PAS spectrum of Nd:glass required a 450 watt xenon arc lamp as a source and 90 minutes to collect whereas Fig. 2b was collected and transformed in under 4 minutes using a 100 watt tungsten-iodide lamp.

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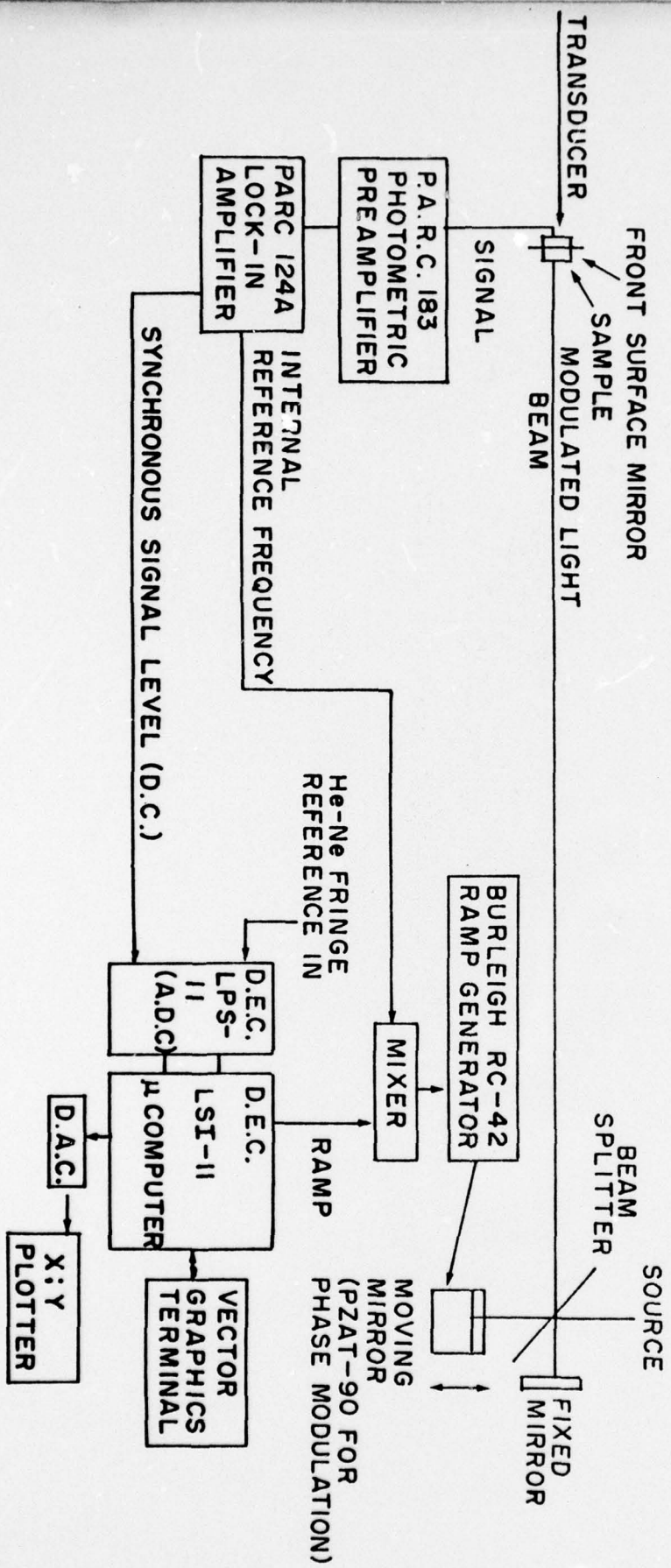[1]A. Rosencwaig, Phys. Today 28, No. 9, 23 (1975).

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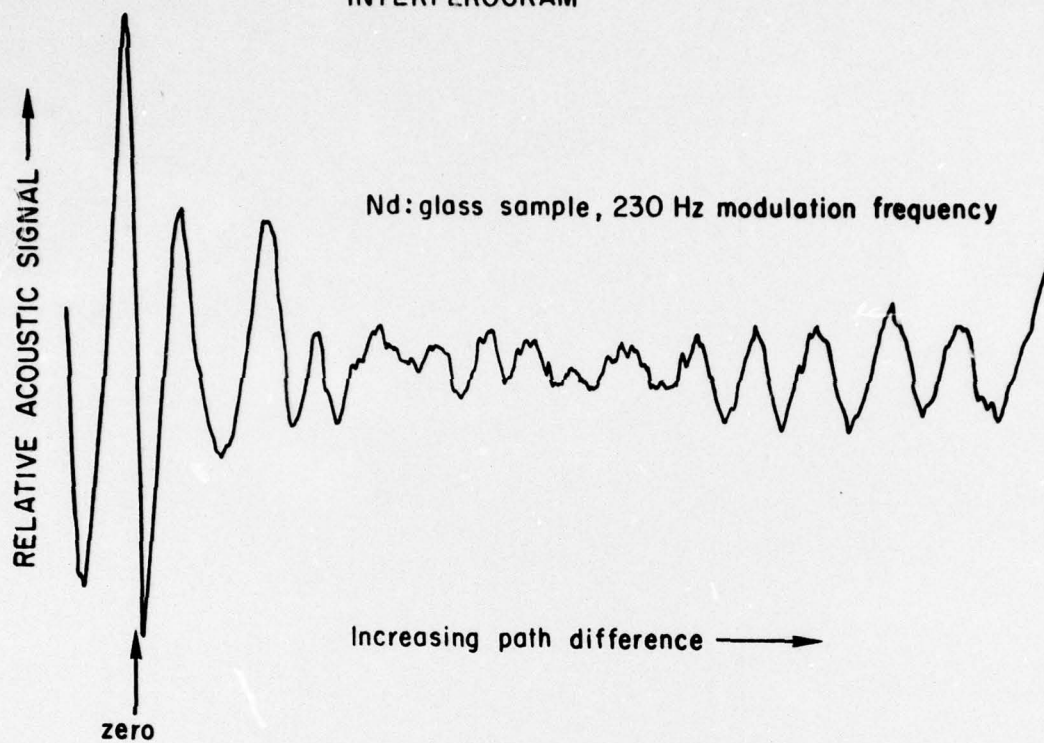
Figure Captions:

FIG. 1.   Schematic of Fourier transform-visible-photoacoustic spectrometer.
A Michelson interferometer is depicted schematically in the top
right hand corner. A He-Ne laser reference system is depicted
that has not been implemented in the present study.

FIG. 2.   Photoacoustic interferogram (above) and absorption spectrum calcu-
lated from the interferogram (below) for a neodymium(III) doped
laser glass sample. The spectrum has not been source normalized
(i.e. signal has not been divided by light source intensity at
each wavelength.) The interferogram was based on samples taken at
256 equally spaced mirror positions. The spectral resolution is
~ 850 cm^{-1} or ~ 20 nm @ $\lambda = 500$ nm.

TRANSDUCER

FRONT SURFACE MIRROR

SAMPLE

MODULATED LIGHT

BEAM

P.A.R.C. 183
PHOTOMETRIC
PREAMPLIFIER

SIGNAL

PARC 124A
LOCK-IN
AMPLIFIER

INTERNAL
REFERENCE FREQUENCY

SYNCHRONOUS SIGNAL LEVEL (D.C.)

He-Ne FRINGE
REFERENCE IN

BURLEIGH RC-42
RAMP GENERATOR

MIXER

D.E.C.
LPS-
11
(A.D.C.)

D.E.C.
LSI-11
μ COMPUTER

RAMP

D.A.C.

X:Y
PLOTTER

VECTOR
GRAPHICS
TERMINAL

BEAM
SPLITTER

SOURCE

MOVING
MIRROR
(PZAT-90 FOR
PHASE MODULATION)

FIXED
MIRROR

INTERFEROGRAM

Nd:glass sample, 230 Hz modulation frequency

RELATIVE ACOUSTIC SIGNAL →

Increasing path difference →

zero

SPECTRUM

Source 100 w quartz lamp
(not normalized)

RELATIVE ACOUSTIC SIGNAL →

WAVELENGTH (NM)

500   900   1300   1700   2100